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(54) Elongate product covering material

(57) A halogen-free and nonflammable covering for electrical cables and the like comprises a blend of ethylene-propylene rubber and copolymers of ethylene with a comonomer proportion of up to 35% by weight or alternatively polyethylene having a density of less than 0.915 g/cc, alone or blended with the copolymers, the blend being filled with a flame-proofing filler and being crosslinkable through the action of moisture by grafting-on unsaturated organosilanes.

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SPECIFICATION

Elongate product covering material

This invention relates to an elongate product covering material which is halogen-free, has been rendered non-flammable by the incorporation in it of one or more flame-inhibiting fillers, and comprises an extruded crosslinked plastics material. The elongate products which may be covered with the material include electrical cables, tube bundle cables and conduits.

Non-flammable mixtures are desired in many industrial fields, for the manufacture of a very wide variety of products. Thus, for example, the polyvinyl chloride insulation of electrical cables and wires must be non-flammable if such cables or wires are to be used in mines, on ships or in other fire-risk or fire-endangered places. Although plasticiser-free polyvinyl chloride is non-flammable, it is not suitable for the production of electrical cables and wires. It is therefore usual to use for this purpose plasticiser-containing polyvinyl chloride, which can still be called flame-resistant.

This latter material is given this property by the hydrogen chloride gas which is liberated in the heat of combustion and which is produced during the decomposition of the polyvinyl chloride insulation and which tends to extinguish flames. It is disadvantageous here, as is known, that damage is produced by gaseous hydrogen chloride which is eliminated on heating and which combines with water or stream to form hydrochloric acid, which etches or destroys metal, concrete and certain other materials. In an attempt to make it possible to suppress such damage, it has already been proposed (DE–OS (German Published Specification) 1,769,343) that very finely divided acid-binding fillers having an average particle size below 250 microns should be added to the polymeric materials, in order to bind the volatile acids eliminated under the action of heat. It has not proved possible, however, for this technique to securely establish itself in practice.

Certain halogen-free base materials which are rendered non-flammable by flame-resistant, halogen-free additives have therefore been adopted. In this connection, a flame-resistant, halogen-free polymer mixture containing a certain amount of aluminium oxide hydrate has been disclosed (DE–OS (German Published Specification) 2,809,294). The base materials here are rubbers or rubber-like materials, which are chemically crosslinked under the action of heat after processing into the final product. Such chemical crosslinking has been practised for some years in "continuous vulcanisation" plants (CV plants) In these, the material to be crosslinked is fed into a tube filled with steam or inert gas. However, this type of crosslinking procedure becomes more and more difficult as the cross-section and therefore the stiffness of the electrical cable or other product increase. Damage to the covering, e.g. the insulation or sheath of a cable, caused by contact of the product passing through the CV plant with the walls of the tube guide cannot always be excluded.

It is furthermore known that a number of polymers which in principle are suitable for the preparation of cable and wire covering materials can be crosslinked using organic silanes. A very wide variety of procedures are possible here, all of which also are actually used in practice. However, when these techniques are applied to mixture compositions with conventional fillers, almost insurmountable problems arise since the quantities of moisture which the fillers themselves introduce can initiate the crosslinking reactions prematurely and in an uncontrolled fashion.

Starting from this prior art, therefore, it is an object of the present invention to provide a halogen-free and non-flammable covering which can be manufactured without problems even for relatively large sheathing cross-sections, but which also meets the mechanical and, if necessary, also the electrical requirements of the respective application, and whose production and processing technology is such as to exclude the above-mentioned disadvantages.

According to the present invention, there is provided an elongate product covering material which is halogen-free, has been rendered non-flammable by the incorporation in it of one or more flame-inhibiting fillers, and comprises an extruded crosslinked plastics material, wherein the plastics material employed comprises (i) an ethylene-propylene rubber and (ii) (a) a copolymer of ethylene with up to 35% by weight of one more comonomers and/or (b) an ethylene polymer having a density less than 0.915 g/cc, and wherein the polymeric materials present have not only been blended with one or more flame-inhibiting fillers but also have been rendered moisture-crosslinkable by virtue of the grafting on of one or more unsaturated organosilanes.

Elongate products of relatively large cross-section can be insulated or sheathed without problems with the present covering material by means of pressureless silane crosslinking, without needing to use complicated CV plants.

The material specified will tolerate the inclusion of an adequate, flame-resistant amount of filler without raising the quality problems, in particular electrical or mechanical quality problems, which have usually arisen in the prior art.

It has been found particularly suitable for the purpose of the invention to blend the ethylene-propylene rubber with ethylene copolymers based on an acetate or acrylate comonomer (e.g.

vinyl acetate) or with polyethylenes having an extremely low density (VLDPE), for example from 0.890 to 0.915 g/cm³. If the ethylene comonomer is an acetate, a proportion of comonomer of 5–35% by weight has proven the most expedient, and if the comonomer is an acrylate, the comonomer proportion is advantageously 5 to 20% by weight.

The ratio of the polymeric components in the blend, i.e. ethylene-propylene rubber to ethylene copolymer or VLDPE, is preferably between 40:60 and 60:40. In order to achieve the flame-resistance desired, appropriate fillers are preferably added to the base blend in an amount of 80–180 parts, more preferably 90–120 parts, per 100 parts of the polymeric materials.

The demand for a halogen-free and nonflammable cable insulation is not easily reconciled with the concurrent demand for good electrical properties. The invention makes it possible to solve this problem by the simultaneous use of two or more polymers. The particularly good electrical properties of the ethylene-propylene rubber (EPR) components are combined with the particularly good mechanical properties of the copolymers or VLDPE, and the good fillability of all components is naturally an additional favourable factor.

It may be found desirable to admix the material with further polymers, additives (e.g. stabilisers against thermal ageing, or against the influence of high-energy irradiation) and processing aids (e.g. lubricants, dispersants and plasticisers), and if appropriate, colouring agents.

The coating material of the invention can be prepared by blending the polymeric components, incorporating the fillers and other additives, more particularly the processing aids and the condensation catalyst, as required, and grafting the one or more silanes on to the polymeric components in separate process steps. After an appropriate period of storage of the material thus prepared, e.g. in the form of a granulate, the final product desired is fabricated in a further process step, being finally subjected, for the purpose of crosslinking, to storage in water, or merely to storage in moist air.

In an advantageous process variant, the polymeric components to be grafted are grafted, either separately or together, without the presence of the fillers, with the one or more organosilanes, and the grafted material is subsequently mixed with the flame-inhibiting filler(s) and the further additives and processing aids, as required, and melted and shaped in the same or in a subsequent procedure. This variant has the advantage of permitting the use of flame-inhibiting fillers which, at elevated temperatures, e.g. graft temperatures of more than 180°C, are liable to decompose to form cleavage products which themselves interfere with the grafting or subsequent crosslinking process in an uncontrolled manner.

The following Examples illustrate the invention. The "parts" mentioned are by weight.

Example 1–The following is a coating material formulation which has been found valuable.

Ethylene-propylene rubber (EPR)	50	parts
Ethylene-vinyl acetate copolymer (vinyl acetate monomer proportion 20% by weight)	50	parts
Flame-inhibiting fillers (aluminium oxide hydrate)	100	parts
Silane (vinyl trimethoxysilane)	2	parts
Peroxide	0.05	part
Condensation catalyst (dibutyltin dilaurate	0.05	part
Plasticiser (naphthenic oil)	10	parts
Lubricants/processing aids (wax)	5	parts
Stabiliser, TMQ (tetramethyldihydroquinoline)	0.4	part

Example 2–The following is a process which has been found valuable.

A: Ethylene/propylene rubber (EPR)	45	parts
Silane	2	parts
Peroxide	0.5	part

Blending of the above is followed by grafting of the EPR.

B: Ethylene-vinyl acetate copolymer (EVA) (vinyl acetate monomer proportion 20% by weight)	100	parts
Silane	2	parts
Peroxide	0.4	part

Blending of the above is followed by grafting of the EVA copolymer.

C:	Filler pre-mix		
	5 parts of EPR and 5 parts of EVA	10	parts
	Aluminium oxide hydrate	120	parts
	Plasticiser	10	parts
	Processing aids	5	parts
	Stabiliser	0.8	part

Compound of the filler pre-mix is followed by a main blending step D, viz:

D:	A	60	parts
	B	40	parts
	C	150	parts
	Catalyst (if appropriate as masterbatch or pre-mix)	0.05	part

Mixing the step D may be immediately followed by a fabrication step, as noted below.

This Example 2 procedure is preferred more particularly in cases in which flame-inhibiting fillers are used (e.g. aluminium oxide hydrates) which eliminate water at elevated temperatures.

In the procedure followed here, the EPR and EVA are each initially grafted with the silane, and the resulting grafted components are thereafter mixed together with the filler pre-mix (C), for example in a cold-mixing step, or when metered into the hopper of a processing extruder. The melting, homogenising and shaping can thus take place in a single operation, the crosslinking of the shaped sheath, the insulation or the like being effected in the course of subsequent storage in water, or simply by allowing the product to be exposed to atmospheric moisture over a relatively long period.

CLAIMS

1. An elongate product covering material which is halogen-free, has been rendered non-flammable by the incorporation in it of one or more flame-inhibiting fillers, and comprises an extruded crosslinked plastics material, wherein the plastics material employed comprises (i) an ethylene-propylene rubber and (ii) (a) a copolymer of ethylene with up to 35% by weight of one or more comonomers and/or (b) an ethylene polymer having a density less than 0.915 g/cc, and wherein the polymeric materials present have not only been blended with one or more flame-inhibiting fillers but also have been rendered moisture-crosslinkable by virtue of the grafting on of one or more unsaturated organosilanes.

2. A material according to claim 1, wherein the said one or more comonomers comprise an acetate comonomer possessing the requisite unsaturation, e.g. vinyl acetate, the proportion of this acetate comonomer being 5 to 35% by weight.

3. A material according to claim 1 or 2, wherein the said one or more comonomers comprise an acrylate comonomer, the proportion of this acrylate comonomer being 5 to 20% by weight.

4. A material according to claim 1, 2 or 3, wherein an ethylene copolymer as specified at "(ii)(b)" is present and this polymer has a density of 0.890 to 0.915 g/cc.

5. A material according to any of claims 1 to 4, wherein the ratio of "(i)" to "(ii)" is 40:60 to 60:40.

6. A material according to any of claims 1 to 5, wherein the plastics material has a flame-inhibiting filler content of 80 to 180 parts by weight per 100 parts by weight of the polymeric materials.

7. A material according to claim 6, wherein the said content is 90 to 120 parts per 100.

8. A material according to any of claims 1 to 7, wherein one or more further polymers, additives, processing aids and/or colouring agents are additionally present.

9. A material according to claim 1, substantially as described in respect of either of the foregoing Examples.

10. A process for the production of a covering according to claim 1 wherein at least one of the polymeric materials employed is grafted with one or more unsaturated organosilanes ahead of being mixed with the one or more flame-inhibiting fillers and such further constituents as are employed, shaping taking place in a subsequent operation.

11. A process according to claim 10, wherein the one or more flame-inhibiting fillers are mixed in in the form of a filler masterbach or pre-mix.

12. A process according to claim 11, wherein the mixing of the filler masterbatch or pre-mix, and the other constituents, melting and shaping into a covering all take place in a single procedure.

13. A process according to claim 10, 11 or 12, wherein a condensation catalyst capable of catalyzing moisture crosslinking is added as a master-batch or pre-mix immediately before the shaping operation.

14. A process according to any of claims 10 to 13, wherein the one or more flame-inhibiting fillers used comprise one or more aluminium oxide hydrates.

15. A process according to any of claims 10 to 14, wherein the one or more flame-inhibiting fillers used comprise magnesium hydroxide alone or blended with an aluminium oxide hydrate.

16. A process as claimed in claim 10, substantially as described in the foregoing Example 2.

17. An elongate product covering material produced by a process as claimed in any of claims 10 to 16.

18. An electrical cable, tube bundle cable or conduit, having a covering composed of a material as claimed in any of claims 1 to 9 or claim 17.

19. A material as claimed in any of claims 1 to 9, or claim 17, or article as claimed in claim 18, wherein the polymeric materials present are not merly moisture-crosslinkable but actually moisture-crosslinked.

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